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(54) Electret

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## **(54) [Name of the Invention]**

### **Electret**

### **Detailed explanation of the Invention**

The present invention is an invention about an electret. In more details, the present invention is an invention about an electret,

- (1) which is formed as a film shaped or sheet shaped material, which is formed from copolymer material obtained from acrylic acid, methacrylic acid or maleic acid and ethylene or styrene, is used, and its two surfaces carry charges with a different sign,
- (2) which is formed as a film shaped or sheet shaped material, which is formed from copolymer material obtained from the metal salt of acrylic acid, methacrylic acid or maleic acid and ethylene or styrene, is used, and its two surfaces carry charges with a different sign.

As an especially appropriate method for the manufacturing of the electret according to the present invention, there is the method according to which there is an electrical insulation material placed on one side of the film, sheet or molded material formed from the above described copolymer material, and a high energy electron beam is irradiated towards the molded material from the side that is opposite to that electrical insulation material, and an electret is produced where the irradiated surface has a positive charge and the opposite surface has a minus charge.

The goal of the present invention is to suggest an electret, which has on its two surfaces electrical charge with opposite signs, and whose electrical charge amount is large, and also, where the attenuation of the electrical charge is small.

In the past, the so-called thermal electretization, has been studied, where an electrical field is applied to a polymer material under heating, and after that it is cooled as it is kept in the state where the electrical field is being applied, and polyethylene, polypropylene, polyvinyl chloride etc., have also been included in the polymer materials, which have been the subject of these studies. Then, regarding the electretization of the vinyl type polymer materials, the incorporation of carboxylic radicals into the polymer material causes a decrease of the electrical properties and especially of the electrical insulation

properties, and from the point of view of the electretization, it has been possible to consider that as an option, which is not preferred.

However, the authors of the present invention have conducted rigorous research and as a result from that they have observed that if the conditions are appropriately selected, an excellent electret is produced from copolymer materials obtained from acrylic acid, methacrylic acid or maleic acid, or their salts, and from ethylene or styrene. Especially, if the electretization treatment is conducted by using electron beam radiation, it is different from the thermal electretization used according to the previous technology and the electretization is achieved through a radiation treatment, which is and is done within an extremely short period of time. And because of that, the characteristics are present that there is no deformation or destruction of the film, sheet, etc., formed products, and not only that, but also, the amount of the electric charge of the obtained electret is extremely high and its electrical charge attenuation is small, and besides that through the selection of the raw materials, it is also possible to impart electric voltage properties and light guide properties. And because of that, this material is extremely useful as a material for audio equipment, like microphones, pick up, speakers, etc., also, it is appropriate in electron copying applications or printing applications, and then in medial field materials, and especially, as materials used in medical instruments which come in contact with blood, etc.

The electret material used according to the present invention is a copolymer material obtained from acrylic acid, methacrylic acid or maleic acid and from ethylene or styrene, or it is a material where a metal ion has been added to the above described copolymer material. However, it is also a good option if copolymer materials are used, which contain correspondingly two types or more of the above described components. Also, it is a good option if the above described copolymer components are used as the main components, and small amounts of other different components are contained as long as it is within the range where there is no deterioration of the properties. In the copolymer material, the amount of the acrylic acid, methacrylic acid or maleic acid is 25 mole % or less, and especially it is preferred that it is 15 mole % or less. Moreover, the term copolymer that is used here includes random, block and conjugated type polymer materials, and besides that it also includes polymer materials obtained by graft copolymerization.

As the electret material according to the present invention, it is possible to use the above described copolymer material by itself, however, then preferably, the composition material is used, which is formed as a metal ion is added to the above described copolymer material. As the metal ion, which is contained in the above described copolymer material used as the electret material according to the present invention, the metals from the Groups I, II, III, VIII from the Periodic Table, especially,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Al}^{+++}$  etc., are preferred.

The above described copolymer material which contains metal ions such as the above described can be produced according to the following method: usually, to a material obtained by the copolymerization of acrylic acid, methacrylic acid or maleic acid and

ethylene or styrene, or to copolymer material, obtained by the graft polymerization of acrylic acid, methacrylic acid or maleic acid onto ethylene or styrene, sodium hydroxide, calcium hydroxide, barium hydroxide, aluminum hydroxide etc., hydroxides of the above described metals, sodium acetate, calcium acetate, zinc acetate, etc., acetic acid salts of the above described metals, calcium oxide, zinc oxide, etc., oxides of the above described metals, barium stearate, calcium stearate, sodium stearate, zinc stearate, etc., high homologous order aliphatic acid salts of the above described metals, metallic zinc etc., above described metals by themselves, are added and mixed. However, for example, these can also be produced according to the method whereby a styrene – acrylic acid copolymer material is dissolved in toluene, and to that a methanol solution of potassium hydroxide is added, and stirred, and in a state where it is a solution to a state where it is close to solution, the neutralization of the carboxylic radical, is conducted. Also, these can be produced according to the method where the neutralized by the above described metal acrylic acid, methacrylic acid or maleic acid is copolymerized with ethylene or styrene.

Moreover, regarding the addition of the metal ion, it is preferred that the incorporated amount be controlled so that the bulk specific resistance of the electretized formed material becomes  $10^{13} \Omega \text{ cm}$  or higher.

The copolymer material used according to the present invention is made into a film, a sheet or a formed material, which is formed and processed from those, and after that an electretization treatment is conducted, and because of that naturally, a molecular weight is necessary to only resist such forming (molding) processes, and it is necessary to obtain a material, which has the appropriate processing properties, namely melting or dissolution properties, however, there is no problem if after the molding it is rendered insoluble and it is not melted. The molecular weight is preferred to be at least 500 or higher, represented by the average polymerization degree.

According to the above described, for the preparation of the electret according to the present invention, an electretization treatment is appropriately applied onto the above described copolymer material, which has been processed into a film, sheet, or closed tubular shape etc., items. As the film forming method, besides the method whereby a solution or a material, which is in a state close to solution, is spread, the melt molding method, especially, the pressure shrinkage molding method, the injection method, the extrusion method, the vacuum molding method, the blowing method, the inflation method, the calendering method, etc., are desirable. It is also possible to add and mix anti-oxidation agents, ultraviolet absorption agents, light stabilization agents, heat stabilization agents, etc., different types of stabilization agents, plasticizers, anti-electrostatic agents, flame retardants, filler agents, lubricants, etc., however, it is preferred that the added amount be controlled so that the electrical resistance of the obtained molded material, namely, the bulk specific resistance becomes  $10^{13} \Omega \text{ cm}$  or lower.

Moreover, the formed material can be non-oriented, uniaxially oriented, biaxially oriented, and all are good options. The thickness of the formed material varies depending

on the electretization method to which it must be subjected, however, for example, in the case when the electretization is conducted by the electron beam radiation treatment, it is desirable that the thickness of the single molded item be 1000 microns or less. And also, even in the case when the molded items are stacked and then treated, it is a good option if the total thickness becomes 5 mm or less. However, if the electron beam radiation conditions are changed and the radiation amount is made to be high, it is also possible to treat materials, which have thickness higher than the above described. In the case when the described below light radiation electretization treatment, thermal electretization treatment are conducted, because of the fact that it is a good option if the applied electrical voltage is constantly normalized relative to the thickness of the molded material, the limit of the thickness of the molded material is determined by the capability of the high electrical voltage generating equipment.

The present invention is an invention about an electret, which has on its two surfaces electrical charge with a different sign, and which is obtained as electron beam radiation, or electrical field, heat, light etc., are applied to a material formed from a copolymer obtained from acrylic acid, methacrylic acid or maleic acid and from ethylene or styrene, and preferably, from the above described copolymer containing a metal ion, and it is electretized. And because of that, here below, the main electretization methods are explained, however, the electretization methods are not limited to these electretization methods.

(i) Electron beam radiation electretization method:

Here the term electron beam has the meaning of an electron beam with energy of 150 kev or higher, and as the radiation device used in practice, there are the Cockroft type electron acceleration device, the Cockroft – Fulton type electron acceleration device, the Van de Graf type electron acceleration device, the resonance transformation device, the linear type electron acceleration device, the Betatrone, the Dynamitron type electron acceleration device, the steel core insulation type electron acceleration device, etc. It is also a good option if there is an electric insulation material on one side of the above described copolymer, or preferably the above described copolymer material containing a metal ion, that has been formed into a film shape, a sheet shape, or a closed tubular shape etc. The irradiation is conducted so that the electron beam is direct relative to the material formed from above described copolymer, and this is achieved as the electron beam is irradiated to the formed material from the side opposite to the side of the electric insulation material, and it is a good option if at this time the distance between the formed material that is being electretized and the electric insulation material is made to be 1 cm or less, and it is also preferred that both materials are intimately adhered. Also, as the material that is being referred to here as the electric insulation material, besides polyethylene, polypropylene, polystyrene, poly tetrafluoroethylene, polycarbonate, polymethyl methacrylate etc., different types of organic materials, also, glass, ceramics etc., inorganic materials, and composite materials formed from both types above, are included. The radiation amount varies depending on the thickness of the formed material

that is subjected to the electretization, the radiation beam resistance properties, or the magnitude of the obtained electrical charge, however, it is preferred that it be within the range from 0.01 to 50 Mrad. The radiation time varies depending on the electron acceleration electrical voltage, the electron beam electric current, etc., however, in order to prevent destruction of the formed materials, it is preferred that it be completed as soon as possible and within several seconds. The electron beam radiation can be conducted in air and under normal temperature and pressure, however, it is also possible to be conducted in vacuum or in inert gas atmosphere like nitrogen or argon gas, and also, it is possible to have heating or light from a light source such as a xenone lamp or mercury lamp, during the time of the radiation.

(ii) Thermal electretization method:

It is the thermal electretization method where alumina foil, etc., conductive material, which becomes a surface electrode is placed in contact with both surfaces of the molded material that is to be electretized, and two electrode conductive bodies are shorted, and by that an electrical voltage is applied, and electrical field is applied to the molded material and it is heated. In the state where the molded material has been subjected to an electrical field and it has been heated for a certain amount of time, it is cooled.

Regarding the electrical voltage, which is applied at this time on both electrode conducting bodies, it is limited to a voltage which will not destroy the insulation of the molded material that is being electretized, and it is a good option if it is high as it goes up to that limit, however, it is preferred that it be from 0.1 to 1000 KV, relative to 1 cm thickness of the molded material. Also, naturally, the heating temperature is limited to the point so there is no melt flow of the molded material, and for the copolymer material, which is used to produce the electret according to the present invention, usually, it is preferred that the temperature be 200°C or lower. Regarding the heating time, it is sufficient if it is maintained at the highest heating temperature for a period of 30 minutes.

(iii) Light radiation electretization method:

Depending on the requirements, it is possible that an electrical field is applied in the copolymer material that is used according to the present invention and by that only it is simply electretized. However, in the case of the electrets such as these, a trend has been observed that it could be stated that the electric charge attenuation is relatively fast. Then, it has been observed that the irradiation of light is effective at the time when the electrical field is being applied. Namely, in order to apply electrical field, electrode, conductive bodies are placed on both surfaces of the molded material that is to be electretized, however, on at least one of the surfaces an electrode formed from transparent electro-conductive material, is placed, and the electrical field is applied as light is being radiated.

Regarding the electrical voltage, which is applied at this time on both electrode conducting bodies, it is limited to a voltage which will not destroy the insulation of

the molded material that is being electretized, and it is a good option if it is high as it goes up to that limit, however, it is preferred that it be from 0.1 to 1000 KV, relative to 1 cm thickness of the molded material. As the light source used in this method, there are the mercury or the xenone lamps. In this case, the illumination at the surface of the material and the time of the light radiation, vary depending on the chemical composition and the thickness of the molded material, the magnitude of the electrical charge to be obtained, etc., however, usually, it is desirable that it be from 5000 Luxes to 1000000 Luxes, and from 1 second to 5 minutes. Moreover, it is also a good option if prior to the electretization treatment according to the light radiation electretization method, an ultraviolet beam etc., is irradiated to the molded material, and the static electricity is eliminated.

The authors of the present invention have conducted all the measurements of the electric properties of the electret after the sample materials have been left for 24 hours in a chamber where the temperature was controlled at 20°C and the humidity was controlled at 65 % RH, and the methods described here below were used to conduct the measurements.

(i) Electric resistance:

The electric resistance was measured by using the high voltage power supply TR-300 B, manufactured by Takeda Research, and a co-oscillation capacity type electric potentiometer TR-84B, a co-ultra-high mega ohm meter and a sample chamber TR-4, were used, and by following the regulations according to JIS.

(ii) Surface electric potential:

A rotary static tester manufactured by Koa Shokai was used. This equipment has been produced in order to measure triboelectricity in the past, however, it was used without the installation of the material subject to the friction.

The sign of the electric charge is was determined from its wave shape when an oscilloscope was attached to this device.

(iii) Surface charge density:

The following two methods were used.

Parallel flat plate condenser: The surface charge density is obtained according to the described here below equation, from the surface electric voltage  $V_A$  (Volts), measured by grounding the back surface of the experimental sample with a copper foil spread over at the experimental sample fixing location of the rotary static tester manufactured by Koa Shokai, and from the separately measured dielectric constant  $\epsilon_s$ .

$$\text{Surface Charge Density: } \rho_s = \frac{V_A \cdot \epsilon_s}{D} \times 0.0855 \times 1.0$$

(Coul/cm<sup>2</sup>)

Here,  $d$  represents the thickness of the molded material (cm),  $\epsilon_s$  represents the value measured by using direct current according to the method that has been reported on pages 144 ~ 147 of the Volume 4 of "Physical Measurement Technology".

Non-polarizing electric current method: The method reported in the "Fibers and Technology" 2 (9), 649 (1970) by Komatsu is used appropriately as is, and it is a method where in the case where the electret is heated as it is in state where both surfaces of the electret are shorted, the amount of the electric current flowing through the circuit is added and the value, which is divided by the electrode area is tabulated.

From the measurement results the described here below is understood.

Even though there are variations depending on the electretization treatment and conditions, for example, if the electron beam radiation electretization method is used, it is possible to easily produce electret where the surface potential is at least 2000 Volts or higher, the surface charge density is from  $10^{-5}$  to  $10^{-7}$  Coul/cm<sup>2</sup>. Regarding this value, when it is compared to the several values that are known relative to electrets, it is from a unit to several units larger, and this indicates that the obtained by this method electret according to the present invention is an excellent electret. Also, it is an electret where the attenuation of the electric charge is slow, and even after the passage of a period of 3 months, there is almost no change from the initial value of the electric charge amount. Also, even after the immersion in water or an aqueous solution of an electrolyte material, the attenuation of the electric charge was low and this is very important characteristic.

Moreover, it is an electret where there is no significant difference generated in the attenuation of the electric charge between the case when after the electretization treatment the obtained electret is stored at a bright location and the case when it is stored at a dark location. And it is considered that is due to the fact that by the electretization of the copolymer material through the electron beam radiation, it becomes a material possessing photoelectric conductive properties.

As it has already been reported, the electretization method by the so-called thermal electretization method whereby an electric field is applied as a vinyl type polymer material, containing polyethylene, polypropylene etc., poly -  $\alpha$ -olefins is being heated, is known. However, there is no known example stating the preparation of a high performance electret obtained from a material such as a vinyl type copolymer material where carboxyl radical, which has been considered to be a material that is not preferred as a material to be incorporated from the point of view stated about the electretization according to the previous technology, or then, carboxyl radical and metal ion, have been incorporated.

Regarding the present invention, it is not only simply an invention about finding an electretization method for the electretization of materials that up to now have been stated to be materials that  $\chi\omicron\upsilon\lambda\delta$  not be electretized, such as copolymers obtained from acrylic



acid, methacrylic acid or maleic acid and ethylene or styrene, and about the preparation of a novel electret. But also, for example, if the electron beam radiation electretization method used in the preparation of the electret according to the present invention is appropriately used on high density polyethylene, only electrets with a surface electric potential of 50 Volts or less, are obtained. And as it is clear from the fact that it is possible to obtain a high electric charge possessing electret, which has 2500 Volts from a polyethylene type copolymer material, that contains 7 mole % of acrylic acid, and where by using  $Zn^{++}$  30 % of its carboxylic radicals, have been neutralized, and from the fact that a low density polyethylene with a bulk specific resistance of  $10^{16} \Omega\text{cm}$ , cannot be electretized at all according to the electron beam radiation electretization method used for the production of the electret of the present invention, however, the above described copolymer material, which contains carboxylic radical, and more preferably contains carboxylic radicals and metal ions, and which is a material with a bulk specific resistance of  $10^{13} \Omega\text{cm}$  or higher, is said to be easily electretized, etc., facts, the ideas defined according to the previous technology have been completely destroyed, and the discovery of the additional result of the incorporation of the carboxylic acid radical or the carboxylic acid radical and the metal ion is very important for the technology.

Then, in the case of the electron beam radiation electretization method and the light radiation electretization method used for the preparation of the electret according to the present invention, compared to the used up to now thermal electretization method, not only are the electretization procedures significantly simplified, but also, the achieved electrical charge of the obtained electret becomes significantly increased, and also, especially, an electret is produced where the radiation surface has a positive electric charge and the opposite surface has a negative electric charge, which is important for the electron beam radiation electretization method, and from this point of view, this is an important characteristic of this method. The fact is that the use of the electron beam radiation electretization method for the preparation of electrets which have negative electric charge on both surfaces is already known for poly tetrafluoro ethylene, polyethylene terephthalate, polycarbonate, however, the preparation of the electret where the radiation surface stably holds a positive electric charge and the surface opposite to that stably holds a negative electric charge, which is obtained according to the method used in the present invention, has not been known at all.

Here below, the present invention will be explained by using practical implementation examples.

### **Practical Example 1**

Ionomer – Sarin “ # 1557 (ethylene – methacrylic acid copolymer material (20 mole % methacrylic acid) containing 2 %  $Zn^{++}$ ), manufactured by Du Pont Company, was made into a film with a thickness of 150 microns by using a heat pressing method, and this was spread over a glass plate, and an electron beam was irradiated in an air atmosphere from the side opposite to the glass plate, by using a Van de Graf type electron acceleration device. The acceleration electric voltage was 8 cm/min, and the radiation dose was 5 Mrad. After the radiation, the film was removed, and the obtained electret was left to

stand for 24 hours in a chamber at a temperature of 20°C and a relative humidity of 65 %, and the static electricity effects etc., were removed and after that when the surface electric potential was measured according to the described above methods, the radiated surface was + 2500 Volts and the opposite surface was –2500 Volts. The surface charge density calculated according to the parallel flat plate condenser method, was  $5.2 \times 10^{-7}$  Coul/cm<sup>2</sup>, and the surface charge density calculated according to the non-polarizing electrode electric current was  $0.9 \times 10^{-6}$  Coul/cm<sup>2</sup>. Moreover, this electret, even after one month, had electric potential of +1500 ~ 200 Volts on the radiated surface and –13090 ~ –1800 Volts on the surface opposite to that.

### **Practical Example 2**

Polyethylene copolymer material obtained by the copolymerization of 15 mole % of methyl methacrylate and 5 mole % of methacrylic acid was ion bridged by using sodium hydroxide. The melt index prior to the addition of the sodium hydroxide was 3.6 g/min, and after the addition, it was 0.16 g/min. The obtained by this method polyethylene copolymer material, containing 1.4 weight % of Na<sup>+</sup>, was made into a film with a thickness of 150 microns by using a heat pressing method, and after that this was uniaxially extruded in air environment at a temperature of 90°C. The orientation ratio was 4 times. This was then spread and adhered over a polyethylene sheet and when it was irradiated by an electron beam of 0.5 Mrad from the side opposite to the polyethylene sheet, an electret was obtained, where the radiated surface carried a positive electric charge and the surface opposite to that carried a negative electric charge. Moreover, electric voltage properties were observed in this electret.

### **Practical Example 3**

Aluminum hydroxide was added to polyethylene copolymer material containing 15 mole % styrene and 5 mole % methacrylic acid, and it was partially made into an aluminum salt, and after that, a film (containing 0.8 weight % Al) with a thickness of 50 microns was produced by using the heat pressing method. To this an ultraviolet light was irradiated for a period of 10 seconds and after that this was placed between nesa glass electrodes, and 1000 Volt electric voltage was applied on both electrodes, and an electric field was applied to the film, and from the side of the plus electrode a light from a xenone lamp was irradiated so that the illumination level at the surface of the experimental material became 120000 Luxes. The time period of the irradiation was 30 seconds. The obtained electret carried an electric charge of +500 Volts on the surface of the side, which was light irradiated, and –460 Volts on the surface of the opposite side.

### **Practical Example 4**

When the same film as that used according to the above Practical Example 3 was used and the radiation by the xenone lamp light source was not conducted, but only an electric field was applied, an electret was obtained, which carried an electric charge of +300 Volts on the surface in contact with the plus electrode, and –420 Volts on the surface of the opposite side, however, after 3 days, there was a decrease to 50 volts or below.

## Practical Examples 5 ~ 8

Different types of films were placed on a polymethyl methacrylate plate, and from the top a 5 Mrad electron beam was irradiated and the results shown according to Table 1, were presented.

**Table 1**

Practical Examples	Radiated Film			Surface Electric Voltage ** (Volts)	
	Material	Type of contained metal ion	Orientation*	Radiated surface	Non-radiated surface
5	Ethylene/vinyl acetate/acrylic acid copolymer (vinyl acetate: 10 mole %, acrylic acid: 20 mole %)	-	NO	+860	-790
6	Ethylene/methacrylic acid copolymer (methacrylic acid: 20 mole %)	Na (3.45 weight %)	UO (x 2.0)	+1200	-1100
7	Ethylene/methacrylic acid copolymer (methacrylic acid: 20 mole %)	Zn (4.9 weight %)	BO (x 3.0 x 3.0)	+2850	-2630
8	Styrene/acrylic acid copolymer (acrylic acid: 10 mole %)	Ca (0.55 weight %)	NO	+520	-580

Moreover, in the case of the Practical Examples 5 ~ 8, the bulk specific resistance of the films was  $10^{13} \Omega\text{cm}$  or higher. In the case of the electret obtained according to the Practical Example 7, when it was stored in a dark box for a period of 1 month, the surface electric potential was 2850 and there was almost no attenuation, however, the one stored in a bright location became 2000 Volts. Then, when light from a xenone lamp was radiated towards the electret obtained according to the Practical Example 7, for a period of 5 minutes, the electric charge became 50 Volts or lower.

## Practical Example 9

From a copolymer material that was obtained as zinc acetate was added (3.2 weight %) to a copolymer consisting of 97 mole % ethylene and 3 mole % anhydrous maleic acid, a film with a thickness of 50 microns was produced by using the pressing method. This film was placed between aluminum foils, and an electrical field of 500 V was applied so that there was no shorting, and it was heated to 90°C. This was maintained for 30 minutes at this state and in the state as the electric field was being applied, the film was

cooled down to a room temperature. And when that was done, an electret was obtained where both surfaces carried electrical charge with different signs.

#### **Practical Example 10**

The film according to the above Practical Example 1 was not spread over a glass plate and the film and the glass were placed at a distance. When the film and the glass plate were placed at a distance of 15 mm, there electretization was not possible, however, in the case when that distance was made to be 5 mm, and in the case when it was made to be 9 mm, electrets were obtained where the surface of the side irradiated by the electron beam radiation carried a positive electric charge and the surface of the opposite side carried a negative charge.

#### **Practical Example 11**

Three pieces of the film obtained according to the Practical Example 6 were stacked and this was then placed on the top of a glass plate and the air in the ambient atmosphere was exchanged with nitrogen, and then to that an electron beam of 0.25 Mrad was irradiated from the side opposite to the glass plate. Electrets were obtained where all of the surfaces of the sides where the electron beam has been projected were positively charged and all the surfaces of the opposite sides were negatively charged.

#### **(57) Scope of the Claims of the Invention**

1. Electret, which is formed as a film shaped or sheet shaped material, which is formed from copolymer material obtained from acrylic acid, methacrylic acid or maleic acid and ethylene or styrene, is used, and its two surfaces carry charges with a different sign.
2. Electret, which is formed as a film shaped or sheet shaped material, which is formed from copolymer material obtained from the metal salt of acrylic acid, methacrylic acid or maleic acid and ethylene or styrene, is used, and its two surfaces carry charges with a different sign.

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62 C 0  
102 K 25  
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⑦ 日本国特許庁

⑧ 特許出願公告

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1

## ⑩ エレクトレット

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## 発明の詳細な説明

本発明は、エレクトレットに関するものである。

さらに詳しくは、本発明は、

(1) アクリル酸、メタクリル酸またはマレイン酸  
とエチレンまたはスチレンとの共重合体から成  
るフィルム状又はシート状体で、その両面が異  
符号の電荷を有するエレクトレット、

(2) アクリル酸、メタクリル酸またはマレイン酸  
の金属塩とエチレンまたはスチレンとの共重合  
体から成るフィルム状又はシート状体で、その両  
面が異符号の電荷を有するエレクトレット、

に関するものである。

本発明のエレクトレットの製造するに特に適し  
た方法は、上記共重合体から作成したフィルム、  
シートまたは成形物の一側に電気絶縁体において、  
電気絶縁体とは反対の側から高エネルギーを有す  
る電子線を成形体に照射し、照射面が正、反対面  
が負の電荷を有するエレクトレットをつくる方法  
である。

本発明の目的は、その両面に反対符号の電荷を  
有し、その電荷量が大きく、かつ電荷の減衰の

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小さいエレクトレットを提供することである。

従来、重合体に対して加熱下で電場をかけ、つ  
いで電場をかけたまま冷却するといういわゆる熱  
エレクトレット化が検討されており、その対象と  
なる重合体中にはポリエチレン、ポリプロピレン、  
ポリ塩化ビニルなども含まれている。そしてビニ  
ル系重合体のエレクトレット化については、重合  
体にカルボキシル基を導入することは、電気的性  
質、とくに電気絶縁性を低下させることになつて  
エレクトレット化という観点からは好ましくない  
ものと考えられてきた。

ところが、本発明者等は鋭意研究の結果、条件  
を適当に選べば、アクリル酸、メタクリル酸また  
はマレイン酸、あるいはこれらの金属塩とエチレ  
ンまたはスチレンとの共重合体からすぐれたエレ  
クトレットをつくり得ることを見出した。とくに  
電子線照射によるエレクトレット化処理を行えば、  
従来の熱エレクトレット化処理とちがつて、  
簡便で、極く短時間の照射処理によつてエレクト  
レット化が達成されるため、フィルム、シートな  
どの成形品を變形、破損させることなく、しかも  
得られたエレクトレットの電荷量が非常に大きい  
こと、その電荷の減衰の少ないことのほかに、原  
材料の選択によつては圧電性や光導電性をも付与  
するという特徴があつて、マイクロホン、ピツ  
クアップ、スピーカなどの音響機器の材料として、  
また電子複写や印刷用の用途に、さらには医療用  
材料、とくに血液と接触する医療器具用材料など  
として極めて有用である。

本発明で使用するエレクトレット材料は、アク  
リル酸、メタクリル酸またはマレイン酸とエチレ  
ンまたはスチレンとの共重合体、あるいは上記共  
重合体に金属イオンを添加したものであるが、上  
記成分をそれぞれ二種以上含んだ共重合体を使用  
してもよい。また、上記共重合成分を主成分とし、  
その特性を損なわない程度に共重合等により他の  
少量成分を含有させてもよい。共重合体中、アク

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リル酸、メタクリル酸またはマレイン酸は25モル%以下、好ましくは15モル%以下が望ましい。なお、ここで共重合体というのは、ランダム、ブロック、交互共重合体のほかに、グラフト共重合させて得た重合体も含まれる。

本発明のエレクトレットの材料としては上記共重合体単独でも使用できるが、好ましくはさらに上記共重合体に金属イオンを添加して成る組成物が使用される。本発明のエレクトレットの材料として使用する上記共重合体に含有させうる金属イオンは、周期律表第I、II、III、VIII族に属するもので、とくに $\text{Na}^+$ 、 $\text{K}^+$ 、 $\text{Ag}^+$ 、 $\text{Cu}^+$ 、 $\text{Cu}^{++}$ 、 $\text{Ca}^{++}$ 、 $\text{Ba}^{++}$ 、 $\text{Zn}^{++}$ 、 $\text{Fe}^{++}$ 、 $\text{Al}^{+++}$ などが望ましい。

このような金属イオンを含有する上記共重合体は、一般的にはアクリル酸、メタクリル酸またはマレイン酸とエチレンまたはスチレンとを共重合させて得たもの、あるいはエチレンまたはスチレンにアクリル酸、メタクリル酸またはマレイン酸をグラフト重合させて得た共重合体に、水酸化ナトリウム、水酸化カルシウム、水酸化バリウム、水酸化アルミニウムなどのような上記金属の水酸化物、酢酸ナトリウム、酢酸カリウム、酢酸亜鉛のような上記金属の酢酸塩、酸化カルシウム、酸化亜鉛のような、上記金属の酸化物、ステアリン酸バリウム、ステアリン酸カルシウム、ステアリン酸ナトリウム、ステアリン酸亜鉛のような上記金属の高級脂肪酸塩、金属亜鉛のような上記金属の単体を添加混練する方法でつくられるが、たとえばスチレン-アクリル酸共重合体をトルエンに溶解し、これに水酸化カリウムのメタノール溶液を添加、攪拌するということに、溶液ないし溶液に近い状態でカルボキシル基の中和を行なう方法でもつくられる。また上記金属イオンで中和したアクリル酸、メタクリル酸またはマレイン酸をエチレンまたはスチレンと共重合させる方法によつてもつくることができる。

なお、金属イオンの添加にあつては、エレクトレット化する成形物の体積固有抵抗が $10^{13}\Omega\text{cm}$ 以上になるように導入量を調節することが望ましい。

本発明に使用する共重合体は、フィルム、シート、あるいはそれらから成形加工される成形物にしてから、エレクトレット化処理を施すので、そ

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うした成形加工に耐えるだけの分子量と、適度の加工性。すなわち溶解あるいは溶解性を有することが必要なことは当然であるが、成形後には不溶不融化しても何らさしつかえない。分子量は、平均重合度で少なくとも500以上が望ましい。

前述の通り、本発明のエレクトレットを得るにはフィルム、シートあるいは封筒状などに成形加工した上記の共重合体にエレクトレット化処理が適用される。成形成膜方法としては、溶液あるいは溶液に近い状態として流延させる方法のほかに、溶融成形法、とくに圧縮成形法、射出成形法、押出し成形法、真空成形法、吹込成形法、インフレーション法、カレンダー法などが望ましい。成形の過程あるいは成形に先立つて、酸化防止剤、紫外線吸収剤、光・熱安定剤など各種安定剤、可塑剤、帯電防止剤、難燃剤、充てん剤、滑り剤などを添加混合することができるが、得られる成形物の電気抵抗すなわち体積固有抵抗が $10^{13}\Omega\text{cm}$ 以下とならないように添加剤の添加量を調節することが望ましい。

なお、成形物は無延伸、一軸延伸、二軸延伸のいずれであつてもよい。成形物の厚みは、これに施すべきエレクトレット化の方法に従つて異なるが、たとえば電子線照射処理によつてエレクトレット化させる場合には、成形物一枚当りの厚みは $1000\mu$ 以下にすることが望ましく、また成形物を重ねあわせて処理する場合にも厚み合計が $5\text{mm}$ 以下になるようにするのがよい。ただし電子線照射条件をかえて照射量を大きくすればこれ以上の厚みを有するものとすることもできる。後述の光照射エレクトレット化処理、熱エレクトレット化処理における場合も、成形物の厚さ当りの印加電圧を一定規準以上にすればよいわけであるから、成形物の厚さの限界は高電圧発生装置の能力によつて決められるわけである。

本発明は、アクリル酸、メタクリル酸またはマレイン酸とエチレンまたはスチレンの共重合体、好ましくは金属イオン含有の上記共重合体の成形物に電子線照射や電場、熱、光などを加えることによつてエレクトレット化して得られ、両面が異符号の電荷を有するエレクトレットに関するものであるから、次に主たるエレクトレット化方法を説明するが、エレクトレット化の方法はこれらの方法だけに限定されるわけではない。

## (I) 電子線照射エレクトレット化法:

ここで電子線というものは150 keV以上のエネルギーを有する電子線を意味し、実際に使用する照射装置としては、コッククロフト型電子加速器、コッククロフト・ワルトン型電子加速器、パン・デ・グラフ型電子加速器、共振変圧器、線型電子加速器、ベータトロン、ダイナミトロン型電子加速器、鉄芯絶縁型電子加速器などがある。フィルム状、シート状あるいは封筒状などに成形加工した上記の共重合体、好ましくは金属イオン含有の上記共重合体の一侧に電気絶縁体をあてがい、電子線が直接上記の共重合体の成形物に当たるように、電気絶縁体の側とは反対の側から成形物に電子線を照射するわけであるが、この際エレクトレット化しようとする成形物と電気絶縁体との距離は1cm以下にするのがよく、両者を密着させるのが最も好ましい。また、ここでいう電気絶縁体の材料としては、ポリエチレン、ポリプロピレン、ポリスチレン、ポリ4フツ化エチレン、ポリカーボネート、ポリメチルメタクリレートなど各種の有機物質以外に、ガラス、セラミックスなどの無機材料、および両者の複合材料も含まれる。照射量は、エレクトレット化しようとする成形物の厚み、耐放射線性、あるいは得ようとする電荷量の大きさなどによつて異なるが、0.01ないし50 Mradの範囲が望ましい。照射時間は、電子加速電圧、電子ビーム電流などによつても異なるが、成形物を破損しないためにはせいぜい数秒程度にとどめることが好ましい。

電子線照射は、空气中、常温常圧下でも行なえるが、真空中、あるいは窒素やアルゴンのような不活性ガス中でも行なうことができ、また照射時に加熱したり、あるいはキセノン灯や水銀灯のような光源からの光を同時照射することもできる。

## (II) 熱エレクトレット化法:

エレクトレット化しようとする成形物の両面にアルミ箔のような面電極となる導体を接触させ、二つの電極導体が短絡しないようにして、これに電圧を印加して、成形物に電場をかけて加熱する。一定時間加熱したら電場をかけたまま成形物を冷却するというのが熱エレクトレット化法である。

この際両電極導体に印加する電圧は、エレクトレット化しようとする成形物の絶縁破壊を生じない限り、どれほど高くてもよいが、成形物の厚さ

1cm当り0.1ないし1000 KVが好ましい。また加熱温度は成形物が熔融流動しない範囲にとどめるべきことは当然であり、本発明のエレクトレットを作るに使用する共重合体については一般的に200℃以下が望ましい。加熱時間は、最高加熱温度に30分間保持すれば十分である。

## (III) 光照射エレクトレット化法:

驚くべきことに、本発明のエレクトレットを作るのに使用しうる共重合体の中には、電場をかけるだけで簡単にエレクトレット化されるものがあるが、このようにして得られたエレクトレットは電荷の減衰が比較的速いという傾向がみとめられる。そこで電場をかける際に、光を照射するのが効果的であることを見出した。すなわち、電場をかけるためにはエレクトレット化しようとする成形物の両面に電極導体を接触させるわけであるが、少なくとも一面だけはネサガラスのような透明導電性材料から成る電極を配置して、光を照射しながら電場をかけるのである。

この際両電極は印加する電圧は、成形物試料の絶縁破壊を生じない限りどれほど高くてもよいわけであるが、成形物の厚さ1cm当り0.1ないし1000 KVの範囲が望ましい。この方法に使用しうる光源としては、水銀灯やキセノン灯などがある。この場合、試料表面における照度および光照射時間は、成形物の化学組成や厚み、得ようとする電荷量の大きさなどによつても異なるが、普通は0.5万ないし100万ルクス、1秒ないし5分程度が望ましい。なお、光照射エレクトレット法によるエレクトレット化処理に先立つて成形物に赤外線などを照射して、静電気を除去しておくのもよい。

本発明者等は、エレクトレットの電気的性質の測定は、すべて20℃、65%RHの温調室内に24時間以上放置した試料について、次の方法を用いて行なつた。

## (I) 電気抵抗:

タケダ理研製ハイ・ボルテージ・パワー・サブライTR-300B、同振動容量型電位計TR-84B、同ウルトラ・ハイ・メガオームメータ及びサンプル・チャンパーTR-42を用いて、JIS規格に準じて測定した。

## (II) 表面電位:

興亜商会製ロータリ・スタチック・テストを用



いた。この装置は本来摩擦静電気を測定するために作られたものであるが、摩擦対象物を取りつけないで使用した。

電荷の符号は、この装置にシンクロスコープを取りつけてその波形から判定した。

(iii) 表面電荷密度：

$$\text{表面電荷密度} : \rho_s = \frac{V_A \cdot \epsilon_s}{d} \times 0.0855 \times 1.0$$

(Coul/cm<sup>2</sup>)

ここでdは成形物の厚み(cm)であり、 $\epsilon_s$ は「物理測定技術」第4巻(朝倉書店)第144~147頁に記載されている方法で、直流を用いて求めた値である。

脱分極電流法：エレクトレットの両面を短絡した状態で、エレクトレットを加熱していく場合に回路に流れる電流量を積算して、電極の面積で割った値をもつて表わす方法で、高松著「繊維と工業」2(9) 649(1970)記載の方法をそのまま適用した。

測定の結果から下記のようなことが解つた。

エレクトレット化の処理や条件によつて違ふが、たとえば電子線照射エレクトレット化法を用いると、表面電位2000ボルト以上、表面電荷密度 $10^{-5}$ ないし $10^{-7}$  Coul/cm<sup>2</sup>というよう25なエレクトレットも容易に作成することができる。こうした値はこれまでに、エレクトレットについて知られている数値に比べて一桁ないし数桁大きいものでこの方法で得られる本発明のエレクトレットがいかに優れたものであるかを示すものであ30る。また電荷の減衰も遅く、3カ月経過時においてもほとんど初期電荷量と変化していないものもある。また水や電解質水溶液に浸漬したあとも、電荷の減衰が少ないことも大きな特徴である。

なお、エレクトレット化処理の後に、得られた35エレクトレットを明るい所に保存した場合と、暗い所に保存した場合とで電荷の減衰に著しい差異を生ずるものがあるが、これは電子線照射によるエレクトレット化によつて共重合体が光電導性をもつようになったためと考えられる。

すでに述べたように、ポリエチレン、ポリプロピレンのようなポリ- $\alpha$ -オレフィンを含むビニル系重合体を加熱しながら電場をかけるいわゆる熱エレクトレット化法でエレクトレット化するこ

\* 次の2通りの方法を用いた。

平行平板コンデンサ法：興亜商会製ロータリ・スタチック・テストの試料固定個所に銅箔を張りつけて試料の裏面が接地されるようにして測定し

5 た表面電位 $V_A$  (ボルト)と、別に測定した誘電

\* 率 $\epsilon_s$ から次式によつて算出した。

とは知られているが、従来エレクトレット化という観点からは好ましくない導入物質であると思われるカルボキシル基、あるいはさらにカルボキシル基と金属イオンとを導入したビニル系共重合体のようなものから高性能のエレクトレットをつくつたという例は知られていない。

本発明は単に、このようなアクリル酸、メタクリル酸またはマレイン酸とエチレンまたはスチレンとの共重合体というこれまでにエレクトレット20化が行なわれていない物質のエレクトレット化法を見い出して新規なエレクトレットを作つたというだけでなく、たとえば本発明のエレクトレットを作るに用いられている電子線照射エレクトレット化法を高密度ポリエチレンに適用すると表面電位50ボルト以下のエレクトレットしか得られないのに、アクリル酸を7モル%含有し、Zn<sup>++</sup>でそのカルボキシル基の30%を中和したポリエチレン系共重合体からは2500ボルトという高電荷量を有するエレクトレットができるという事実や、体積固有抵抗が $10^{16}$   $\Omega$ cmの低密度ポリエチレンは、本発明エレクトレットを作るに用いられる電子線照射エレクトレット化法によつて全くエレクトレット化されないのにカルボキシル基より好ましくはカルボキシル基と金属イオンとを含有する前記の共重合体は体積固有抵抗 $10^{13}$   $\Omega$ cm以上のものが容易にエレクトレット化されるという事実などからもわかるように、従来の固定概念を全く打ち破る。カルボキシル基、あるいはカルボキシル基と金属イオンとの導入添加効果を見い40出したところに大きな意義がある。

さらに本発明のエレクトレットを作るに用いられる電子線照射エレクトレット化法や光照射エレクトレット化法は、これまでの熱エレクトレット化法に比べて、エレクトレット化操作を大幅に簡



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略化させるだけでなく、得られたエレクトレットの到達電荷量を著しく高めたことになり、またとくに電子線照射エレクトレット化法について重要なことは、照射面が正の電荷をもち、反対面が負の電荷をもつたエレクトレットを作成し得ることであつて、この点にこの方法の大きな特徴がある。なぜなら電子線照射エレクトレット化法によつて両面が負の電荷をもつエレクトレットの作成はすでにポリ4フッ化エチレン、ポリエチレンテレフタレート、ポリカーボネートについて知られてい

るが、本発明において使用される方法で得られるような照射面が正、反対面が負の電荷を安定に保持するようなエレクトレットの作成は全く知られていないからである。

以下、本発明の実施例について説明する。

#### 実施例 1

Du Pont社製アイオノマー・サーリン® #1557(エチレン-メタクリル酸共重合体(メタクリル酸20モル%)Zn+2%含有)を熱プレス法で厚さ150μのフィルムにし、これをガラス板に張りつけて空気中でバンデグラフ型電子加速器を用いてガラス板とは反対の側から電子線を照射した。加速電圧は1 MeV、ビーム電流は100 μA、ベルト走行速度は8 cm/minで、照射量は5 Mradであつた。照射後フィルムをはがし、得られたエレクトレットを20℃、65%RHの温調室に24時間放置して静電気などの影響を除去してから、前に記載した方法で表面電位を測定したところ照射面が+2500ボルト、反対面が-2300ボルトであつた。平行平板コンデンサ法に従つて計算した表面電荷密度は $5.2 \times 10^{-7}$  Coul/cm<sup>2</sup>で、脱分極電流で求めた表面電荷密度 $0.9 \times 10^{-6}$  Coul/cm<sup>2</sup>であつた。このエレクトレットは1カ月後もなお照射面が+1500~2000ボルト、反対側面が-1300~1800ボルトの電位を有していた。

#### 実施例 2

メタクリル酸メチル15モル%及びメタクリル

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酸5モル%と共重合したポリエチレン共重合体を水酸化ナトリウムによつてイオン架橋した。メルトインデックスは水酸化ナトリウム添加前が3.6 g/min、添加後が0.16 g/minであつた。こうして得たNa+1.4重量%含有ポリエチレン共重合体を熱プレスで厚さ150μのフィルムにしてから、これを90℃の空気浴中で一軸延伸した。延伸倍率は4倍であつた。これをポリエチレンのシートに張りつけてポリエチレンシートとは反対側から0.5 Mradの電子線を照射したところ、照射面が正、反対面が負の電荷をもつエレクトレットが得られた。なおこのエレクトレットには、圧電性がみとめられた。

#### 実施例 3

スチレン15モル%、メタクリル酸5モル%を含むポリエチレン共重合体に水酸化アルミニウムを加え、部分的にアルミニウム塩とした後、熱プレス法によつて厚さ50μのフィルム(A<sub>2</sub>O<sub>3</sub> 0.8重量%含有)を作成した。これに赤外線を10秒間照射してから、両面からネサガラス電極ではさみ、両電極に1000ボルトの電圧を印加してフィルムに電場をかけ、プラス電極側からキセノン灯の光を照射し試料表面での照度が12万ルクスになるようにした。照射時間は30秒であつた。得られたエレクトレットは、光が照射された側の面が+500ボルト、反対側の面が-460ボルトの電荷をもつていた。

#### 実施例 4

実施例3に用いたと同様なフィルムをキセノン灯光源で照射をしないでただ電場のみをかけたところ、プラス電極に接した面が+300ボルト、反対面が-420ボルトの電荷をもつエレクトレットが得られたが、3日後には50ボルト以下に減衰した。

#### 実施例 5~8

種々のフィルムをポリメチルメタクリレート板上に置いて、上方から5 Mradの電子線を照射し表1の結果を得た。

表 1

実施例	照 射 フ イ ル ム			表面電位 <sup>※※</sup> (ボルト)	
	材 質	含有金属の種類	延 伸 <sup>※</sup>	照射面	非照射面
5	エチレン/酢ビ/ アクリル酸共合体 (酢ビ:10モル%, アクリル酸:20モル%)	—	NO	+860	-790
6	エチレン/メタクリル酸 共重合体 (メタクリル酸:20モル%)	Na (3.45重量%)	UO (×2.0)	+1200	-1100
7	エチレン/メタクリル酸 共重合体 (メタクリル酸:20モル%)	Zn (4.9重量%)	BO (×3.0×3.0)	+2850	-2630
8	スチレン/アクリル酸 共重合体 (アクリル酸:10モル%)	Ca (0.55重量%)	NO	+520	-580

※ NOは無延伸、UOは一軸延伸、BOは二軸延伸を、またカッコ内はたて及びよこの延伸倍率を表わす。

※※ 電子線照射によるエレクトレット化処理後2日目のエレクトレットの表面電位を表わす。

なお実施例5～8は、フィルムの体積固有抵抗が $10^{13} \Omega \text{cm}$ 以上であつた。実施例7のエレクトレットを、暗箱中で1カ月間保存したところ表面電位は2850ボルトとほとんど減衰していなかつたが、明るい所で保存したものは2000ボルトになつてた。さらに実施例7のエレクトレットにキセノン灯の光を5分間照射したところ電荷は50ボルト以下になつた。

#### 実施例 9

エチレン97モル%、無水マレイン酸3モル%から成る共重合体に、酢酸亜鉛を添加して(3.2重量%)できた共重合体からプレス法で厚さ50μのフィルムを作成した。このフィルムをアルミ箔の間にはさみ、短絡しないようにして500Vの電場をかけ、90℃まで加熱した。30分間の状態に保ち、電場をかけたままフィルムを室温まで冷却したところ、フィルム両面が異符号の電荷を有するエレクトレットが得られた。

#### 実施例 10

実施例1においてフィルムをガラス板に張付けないで、フィルムとガラス板とを離して配置した。フィルムとガラス板との距離を15mmとするとエレクトレット化できなかつたが、5mmとした場合には、電子線照射で照射した側の面が正、反対側の面が負の電荷をもつエレクトレットが得られた。

#### 実施例 11

実施例6で用いたフィルムを3枚重ねて、ガラス板上に置き雰囲気を変換してこれにガラス板とは反対の側から0.25Mradの電子線を照射した。電子線が投射されてきた側の面がいずれも正反対側の面がいずれも負に帯電したエレクトレットが得られた。

#### ⑦特許請求の範囲

1 アクリル酸、メタクリル酸またはマレイン酸とエチレンまたはスチレンとの共重合体から成るフィルム状又はシート状体で、その両面が異符号の電荷を有するエレクトレット。

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2 アクリル酸、メタクリル酸またはマレイン酸の金属塩とエチレンまたはスチレンとの共重合体から成るフィルム状又はシート状体で、その両面が異符号の電荷を有するエレクトレット。

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⑨引用文献

特 公 昭40-7394

